Sworn English translation of the Provisional Application No. 60/292,923 filed May 24, 2001.

DECLARATION

I, Jun OKAMOTO, residing at 2023, Takao-machi, Hachioji-shi, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/292,923 filed on May 24, 2001.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 11th day of September, 2002

Jun Okamoto

Jun OKAMOTO

[Document Name] Specification

[Title of the Invention] Coated Zinc Oxide Particle, and Production Process and Applications thereof

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to zinc oxide employed in resin products, rubber products, paper products, cosmetics, pharmaceutical products, paint, printing ink, ceramic products, electronic parts, etc., and more particularly to coated zinc oxide particles exhibiting excellent dispersibility in resin; to a thermoplastic resin composition containing the particles, the composition being endowed with excellent visible light transmission property and ultraviolet ray shielding property; to a molded product formed from the composition; and to production processes for the particles, the composition, and the molded product.

[0002]

[Background Art]

Zinc oxide, also called zinc flower, has long been known as a white pigment. Zinc oxide exhibits the following optical properties. When zinc oxide is formed into fine particles having a diameter approximately half the wavelength of visible light, the particles allow visible light to pass therethrough since the scattering effect of the zinc dioxide particles is reduced considerably, and selectively absorb ultraviolet rays by virtue of the excellent ultraviolet

absorbing effect of zinc oxide.

[0003]

Conventionally known ultraviolet absorbers include organic ultraviolet absorbers such as benzophenone-based absorbers, benzotriazole-based absorbers, salicylate-based absorbers, and substituted-acrylonitrile-based absorbers. However, a limitation is imposed on use of such an ultraviolet absorber, from the viewpoint of safety. Meanwhile, when such an ultraviolet absorber is incorporated into a thermoplastic resin or a similar material and the resultant mixture is subjected to molding, the absorber is decomposed because of its poor heat resistance or undergoes bleedout during molding. Therefore, zinc oxide particles exhibiting excellent safety and high heat resistance have become of interest as a replacement for organic ultraviolet absorbers.

[0004]

Regarding ultraviolet absorbers containing such zinc oxide particles, Japanese Patent Application Laid-Open (*kokai*) No. 5-171130 discloses a resin molded product in which zinc oxide fine powder having a particle size of 0.1 μm or less is incorporated into a transparent resin. Japanese Patent Application Laid-Open (*kokai*) Nos. 5-295141 and 11-302015 disclose zinc oxide fine particles which are coated with a silicon compound, in order to reduce impairment of weather resistance of the fine particles attributable to the photocatalytic effect, and to improve dispersibility of the

fine particles in a resin.

[0005]

[Problems to be Solved by the Invention]

However, conventional zinc oxide particles produced through the techniques disclosed in the above publications aggregate considerably and are difficult to disperse uniformly in a resin. Therefore, the resultant resin composition becomes turbid, and does not necessarily exhibit sufficient transparency.

[0006]

The present invention contemplates provision of coated zinc oxide particles exhibiting excellent dispersibility in resin; a thermoplastic resin composition containing the particles, the composition being endowed with excellent visible light transmission property and ultraviolet ray shielding property; a molded product formed from the composition; and production processes for the particles, the composition, and the molded product.

[0007]

[Means for Solving the Problems]

The present inventors have performed extensive studies, and have attained the above objects by coating zinc oxide particles with metallic soap.

Accordingly, the present invention provides the following.

(1) A process for producing zinc oxide particles coated with a metallic soap, characterized by comprising mixing zinc

oxide particles with a metallic soap at a temperature equal to or higher than the melting point of the metallic soap.

[0008]

(2) Coated zinc oxide particles produced through the process as recited in (1).

(3) Coated zinc oxide particles in which the surfaces of zinc oxide particles are coated with a metallic soap.

(4) Coated zinc oxide particles according to (2) or (3), wherein zinc oxide has an average primary particle size of 0.005 to 0.1 μm.

(5) Coated zinc oxide particles according to any one of (2) through (4), wherein the metallic soap is a metallic salt of at least one fatty acid selected from the group consisting of lauryl acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, behenic acid, montanic acid, and derivatives thereof.

(6) Coated zinc oxide particles according to any one of (2) through (4), wherein the metallic soap is at least one species selected from the group consisting of zinc stearate, magnesium stearate, and calcium stearate.

(7) Coated zinc oxide particles according to any one of (2) through (6), wherein zinc oxide particles have siloxane bonding on the surfaces thereof.

[0009]

(8) A thermoplastic resin composition comprising coated zinc oxide particles as recited in any one of (2) through (7).

(9) A thermoplastic resin composition according to (8), which

assumes the form of a compound or masterbatch.

(10) A thermoplastic resin composition according to (8), wherein the amount of the zinc oxide particles falls within a range of 0.01 to 80 mass% on the basis of the entirety of the composition.

[0010]

(11) A molded product formed through molding of a thermoplastic resin composition as recited in any one of (8) through (10).

(12) A molded product according to (11), which is at least one species selected from among fiber, film, and plastic molded products.

[0011]

(13) A process for producing a thermoplastic resin composition as recited in any one of (8) through (10), which comprises employing coated zinc oxide particles as recited in any one of (2) through (7).

(14) A process for producing a molded product as recited in (11) or (12), which comprises employing a thermoplastic resin composition as recited in any one of (8) through (10).

[0012]

[Modes for Carrying Out the Invention]

As used herein, the term "metallic soap" refers to a salt of a fatty acid having 10 or more carbon atoms, among metal-containing fatty acid salts. Examples of the metallic soap include metallic salts of lauryl acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid,

behenic acid, montanic acid, derivatives thereof, etc. Examples of the element constituting the metallic salt include magnesium, zinc, barium, calcium, and aluminum. Of these metallic soaps, for example, zinc stearate, magnesium stearate, or calcium stearate is preferred, since it exerts an excellent effect of improving dispersibility of zinc oxide particles in a resin.

[0013]

No particular limitation is imposed on the zinc oxide particles employed in the present invention, so long as the particles predominantly contain zinc oxide, and exhibit the aforementioned optical properties. No particular limitation is imposed on the method for producing zinc oxide employed as a raw material in the present invention, and the zinc oxide may be produced through any of a French method, an American method, and a wet method. The zinc oxide particles preferably have an average primary particle size of 0.001 to 0.2 μm, more preferably 0.005 to 0.1 μm. When the average primary particle size is 0.001 μm or less, efficient production of the particles becomes difficult, whereas when the average primary particle size exceeds 0.2 μm, a resin containing coated zinc oxide particles formed of the particles may fail to exhibit sufficient transparency.

[0014]

In order to impart properties such as weather resistance and electrical conductivity to a resin containing the coated zinc oxide particles, in the present invention,

zinc oxide particles which have undergone surface treatment may be employed as a raw material. For example, in order to improve the weather resistance of a resin containing the coated zinc oxide particles, zinc oxide particles having siloxane bonding on the surfaces thereof may be employed. Examples of the zinc oxide particles having siloxane bonding include zinc oxide particles coated with silica, silicone, alkoxysilane, etc. Examples of the coating method include, but are not limited to, a method in which zinc oxide particles are dry-mixed with silicone or alkoxysilane; and a method in which zinc oxide particles are added to a sodium silicate aqueous solution, and the resultant solution is neutralized with hydrochloric acid or sulfuric acid, followed by filtration, washing, and drying.

[0015]

The coated zinc oxide particles of the present invention are produced by mixing zinc oxide particles with a metallic soap by use of, for example, a high-speed mixer at a temperature equal to or higher than the melting point of the metallic soap. Thus, when zinc oxide particles are mixed with a metallic soap at a temperature equal to or higher than the melting point of the metallic soap, the zinc oxide particles are uniformly coated with the metallic soap.

[0016]

When zinc oxide particles are mixed with a metallic soap at a temperature lower than the melting point of the metallic soap, uniform coating of the particles with the

metallic soap is difficult to attain, and improvement in dispersibility of the particles in a resin may fail to be attained. When coated zinc oxide particles are to be incorporated into the below-described resin, the amount of the metallic soap is preferably 0.1 to 50 mass%, more preferably 1 to 20 mass%, on the basis of the entirety of the zinc oxide particles. When the amount is less than 0.1 mass%, the zinc oxide particles fail to exhibit good dispersibility in the resin, whereas when the amount exceeds 50 mass%, there arise problems such as occurrence of bleedout and generation of soot during molding.

[0017]

The zinc oxide particles of the present invention may be incorporated into a thermoplastic resin, to thereby prepare a thermoplastic resin composition. Specific examples of the thermoplastic resin include polyethylene, polypropylene, polystyrene, polyethylene terephthalate, AS resin, ABS resin, AES resin, polyvinylidene chloride, methacrylic resin, polyvinyl chloride, polyamide, polycarbonate, polyallyl ester, polyimide, polyacetal, polyether ketone, polyether sulfone, polyphenyl oxide, and polyphenylene sulfide.

[0018]

The thermoplastic resin composition containing the zinc oxide particles of the present invention may be employed in the form of a compound, masterbatch, etc. The amount of the zinc oxide particles in the thermoplastic resin composition

is 0.01 to 80 mass%, preferably 1 to 50 mass%, on the basis of the entirety of the composition. The thermoplastic resin composition may contain additives such as an antioxidant and an antistatic agent.

[0019]

In the present invention, the aforementioned thermoplastic resin composition is subjected to molding, to thereby form a molded product exhibiting ultraviolet shielding property. Examples of the molded product include fiber, film, and plastic molded products.

[0020]

[Examples]

The present invention will next be described in detail by way of Examples, which should not be construed as limiting the invention thereto.

[0021]

Example 1:

Zinc oxide particles (size of primary particles: 0.03 μm) (UFZ-40, product of Showa Titanium Co., Ltd.) (20 kg) and zinc stearate (Zinc Stearate S, melting point: 120°C, product of NOF Corporation) (2 kg) were placed in a 300-liter high-speed stirring mixer (Super Mixer SMG-300, product of KAWATA MFG Co., Ltd.). Subsequently, the resultant mixture was mixed at an impeller peripheral speed of 20 m/s while being heated from the outside by use of steam, until the temperature of the resultant powder became 140°C. Subsequently, the powder was left to cool, to thereby yield

zinc oxide particles coated with zinc stearate.

[0022]

Subsequently, by use of a small-sized twin-screw kneading extruder having a size of 15 mm (KZW15-30MG, product of Technovel Corporation), the zinc oxide particles coated with zinc stearate (22 parts by mass) and low-density polyethylene (Jrex JH607C, product of Japan Polyolefins Co., Ltd.) (78 parts by mass) were melt-kneaded at 150°C, and pelletized at an extrusion rate of 1 kg/hr, to thereby produce a low-density polyethylene columnar compound (1 kg) containing zinc oxide particles, each having a diameter of 1 mmϕ, a length of 3 to 5 mm, and a weight of 0.003 to 0.01 g. When the compound (1 kg) was produced, a stainless-steel mesh of 45 μm was mounted on a breaker plate of the twin-screw kneading extruder, and an increase in pressure was measured. As a result, the pressure was increased by only 0.5 MPa, and the zinc oxide particles coated with zinc stearate were found to be uniformly dispersed in the low-density polyethylene.

[0023]

Subsequently, the above-produced low-density polyethylene compound containing the zinc oxide particles (200 g) and low-density polyethylene (Jrex F6200FD, product of Japan Polyolefins Co., Ltd.) (1,800 g) were mixed together for 10 minutes by use of a V-type blender (RKI-40, product of Ikemoto Scientific Technology Co., Ltd.), to thereby prepare a pellet mixture.

[0024]

Subsequently, the resultant pellet mixture was subjected to extrusion by use of a small-sized twin-screw kneading extruder having a T die of 200 mm (KZW15-30MG, product of Technovel Corporation), at a die temperature of 250°C, to thereby form a film having a thickness of 80 μm. The resultant low-density polyethylene film was subjected to measurement of transmittance by use of a spectrophotometer (UV-2400PC, product of Shimadzu Corporation). Transmittance at 360 nm was found to be 0%, and transmittance at 550 nm was found to be 90%. The results are shown in Table 1. When the polyethylene film becomes turbid so as to reduce transparency thereof, the transmittance of the film is lowered. Therefore, the transmittance of the film at 550 nm is employed as an index of transparency.

[0025]

Example 2:

The procedure of Example 1 was repeated, except that the zinc stearate was replaced by calcium stearate (Ca-St, melting point: 152°C, product of Nitto Chemical Industry Co., Ltd.), and mixing was carried out under heating at 160°C by use of the high-speed stirring mixer. The results are shown in Table 1.

[0026]

Example 3:

The procedure of Example 1 was repeated, except that the zinc stearate was changed to magnesium stearate (Mg-St, melting point: 123°C, product of Nitto Chemical Industry Co.,

Ltd.), and mixing was carried out under heating at 140°C by use of the high-speed stirring mixer. The results are shown in Table 1.

[0027]

Example 4:

Zinc oxide particles (size of primary particles: 0.03 μm) (UFZ-40, product of Showa Titanium Co., Ltd.) (20 kg) were placed in a 300-liter high-speed stirring mixer (Super Mixer SMG-300, product of KAWATA MFG Co., Ltd.), and then mixed at an impeller peripheral speed of 10 m/s. Subsequently, silicone having siloxane bonding (AFP-1, product of Shin-Etsu Chemical Co., Ltd.) (600 g) was sprayed through a two-fluid nozzle onto the zinc oxide particles in the mixer. Thereafter, the resultant zinc oxide particles were mixed at an impeller peripheral speed of 20 m/s while being heated from the outside by use of steam, until the temperature of the resultant powder became 140°C. Subsequently, the powder was left to cool, to thereby yield zinc oxide particles coated with silicone.

The resultant silicone-coated zinc oxide particles were coated with zinc stearate in a manner similar to that of Example 1, and subsequently, a low-density polyethylene film containing the zinc oxide particles was formed in a manner similar to that of Example 1. The results are shown in Table 1.

[0028]

Comparative Example 1:

The procedure of Example 1 was repeated, except that zinc oxide particles (size of primary particles: 0.03 μm) (UFZ-40, product of Showa Titanium Co., Ltd.) were not coated with zinc stearate, to thereby form a low-density polyethylene film containing the zinc oxide particles. The results are shown in Table 1.

[0029]

Comparative Example 2:

The silicone-coated zinc oxide particles obtained in Example 4 were not coated with zinc stearate, and a low-density polyethylene film containing the zinc oxide particles was formed in a manner similar to that of Example 1. The results are shown in Table 1.

[0030]

Comparative Example 3:

The procedure of Example 1 was repeated, except that mixing was carried out under heating at 100°C by use of the high-speed stirring mixer. The results are shown in Table 1.

[0031]

Comparative Example 4:

Zinc oxide particles (size of primary particles: 0.03 μm) (UFZ-40, product of Showa Titanium Co., Ltd.) (400 g), zinc stearate (Zinc Stearate S, melting point: 120°C, product of NOF Corporation) (40 g), and low-density polyethylene (Jrex JH607C, product of Japan Polyolefins Co., Ltd.) (1,560 g) were mixed together for 10 minutes by use of a V-type blender (RKI-40, product of Ikemoto Scientific Technology Co.,

Ltd.). The resultant mixture was kneaded by use of a small-sized twin-screw extruder in a manner similar to that of Example 1, and subsequently, a low-density polyethylene film containing the zinc oxide particles was formed in a manner similar to that of Example 1. The results are shown in Table 1.

[0032]

Comparative Example 5:

Low-density polyethylene (Jrex JH607C, product of Japan Polyolefins Co., Ltd.) was melt-extruded at 150°C and at an extrusion rate of 1 kg/hr by use of a small-sized twin-screw kneading extruder having a size of 15 mm (KZW15-30MG, product of Technovel Corporation), to thereby produce columnar pellets (1 kg), each having a diameter of 1 mmϕ, a length of 3 to 5 mm, and a weight of 0.003 to 0.01 g. During pelletization, in a manner similar to that of Example 1, a stainless-steel mesh of 45 μm was mounted on a breaker plate of the twin-screw kneading extruder, and an increase in pressure was measured.

[0033]

Subsequently, the above-produced low-density polyethylene pellets were subjected to extrusion by use of a small-sized twin-screw kneading extruder having a T die of 200 mm (KZW15-30MG, product of Technovel Corporation) at a die temperature of 250°C, to thereby form a film having a thickness of 80 μm. The resultant low-density polyethylene film was subjected to measurement of transmittance by use of

a spectrophotometer (UV-2400PC, product of Shimadzu Corporation). The results are shown in Table 1.

[0034]

[Table 1]

	Siloxane bonding on the surface of zinc oxide fine particles	Metallic soap		Heating-mixing temperature	Increase in pressure during melting-kneading	Transmittance of film	
		Type	Melting point			360 nm	550 nm
Ex. 1	No	Zinc stearate	120°C	140°C	0.5 Mpa	0%	90%
Ex. 2	No	Calcium stearate	152°C	160°C	1.5 Mpa	1%	82%
Ex. 3	No	Magnesium stearate	123°C	140°C	1.0 Mpa	1%	86%
Ex. 4	Yes	Zinc stearate	120°C	140°C	0.3 Mpa	0%	92%
Comp. Ex. 1	No	None	-	-	28 Mpa	15%	70%
Comp. Ex. 2	Yes	None	-	-	14 Mpa	5%	74%
Comp. Ex. 3	No	Zinc stearate	120°C	100°C	8.0 Mpa	3%	77%
Comp. Ex. 4	No	Zinc stearate	120°C	Room temperature	10 Mpa	3%	75%
Comp. Ex. 5	-	-	-	-	0 Mpa	94%	95%

[0035]

[Effects of the Invention]

The present invention provides zinc oxide particles coated with a metallic soap, which exhibit excellent dispersibility in resin; a thermoplastic resin composition containing the particles, the composition being endowed with excellent visible light transmission property and ultraviolet ray shielding property; a molded product formed from the composition; and production processes for the particles, the composition, and the molded product.